UDC 666.1.031.1:666.171:666.125:666.1.01

EFFECT OF THE REDOX POTENTIAL OF THE GLASS BATCH AND CULLET ON THE TINTING OF INDUSTRIALLY PRODUCED GLASS CONTAINING IRON OXIDES

N. F. Zhernovaya,[1] N. I. Min'ko,[1] V. I. Onishchuk,[1] and L. I. Mel'nikova[1]

Translated from Steklo i Keramika, No. 3, pp. 11 – 12, March, 2000.

The effect of the redox potential of the glass batch and cullet on the tint of industrially produced glasses containing up to 0.5% iron oxides is studied. The batch redox boundaries making it possible to obtain glass of green, bluish-green, yellow-green, and brown tints are delineated. The obtained results make it possible to predict the tint and tint shade of glass at the stage of batch preparation.

One of the main technological parameters determining the efficiency of glass melting, the redox processes in glass melts, and the pigmentation and decolorization of glass is the redox potential (ROP) of the glass batch [1 – 3].

Mass-produced glasses containing up to 0.5% iron oxides (semiwhite, green, and brown container glass, heat-absorbing sheet glass) are sensitive to variations in the batch ROP. Fluctuations in the content of oxidizing or reducing agents in the batch can shift the equilibrium between the iron oxides and other elements of variable valence, which complicates the melting and molding processes and makes the glass tint unstable.

At the same time, maintenance of a constant value of the ROP makes it possible to stabilize the indicated technological parameters and control the glass tint at the stage of batch preparation.

At present, this parameter usually is not controlled and is largely ignored at most glass factories. There are no specific recommendations in the literature regarding batch ROP values to be maintained in melting iron-containing glasses of various tints: green and brown (container glass), light blue (heat-absorbing). As a result, the batch ROP values at most glass factories are unsatisfactory and melting is not stable. The ROP of batches for both green and brown glasses have positive (oxidizing) values (from + 30 to + 80), whereas it is necessary to develop a negative (reducing) potential in batches for brown glass [2].

The effect of glass cullet added to the batch on the ROP is virtually not studied, although the current tendency is to increase the recycled-cullet content, especially in making container glass [4].

The authors investigated the effect of the batch ROP on the color of glass of the following composition (wt.%): 72.0 SiO_2, 1.6 Al_2O_3, 9.0 CaO, 3.8 MgO, 13.6 Na_2O, 0.4 Fe_2O_3 (above 100%). Traditional raw materials were used for batch preparation: sand, alumina, dolomite, chalk, soda, sodium sulfate, saltpeter, and coal. Iron oxide was introduced as hematite (mixtures 1 – 6) and metallic iron powder (mixture 7). The ROP of the batches was varied over a wide range from + 168.5 to – 121.1 by varying the content of the oxidizers (saltpeter and sodium sulfate) and the reducing agent (coal). The batch ROP was determined based on the ROP of the raw materials calculated taking into account their decomposition reactions at high temperatures [1, 2] (Table 1).

The glasses were melted in two stages in 150 ml corundum crucibles in a laboratory resistive electric furnace with silicon carbide heaters under constant temperature and time conditions (1400°C, 2 h). Thus, the effect of factors other than the batch ROP on the glass tint was excluded.

After a 2 h hold, the melts were cast into molds on a metal plate, and the molded samples were annealed in a laboratory muffle furnace.

TABLE 1

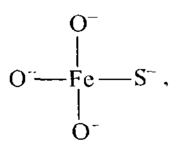
Batch	Weight content of Na_2O, % (of its total content in glass), introduced in			Weigh content of coal, % (of sodium sulfate content)	ROP
	soda	saltpeter	sodium sulfate		
1	50	50	–	–	+ 168.5
2	75	25	–	–	+ 83.8
3	85	–	15	6	+ 35.5
4	85	–	15	12	– 16.8
5	85	–	15	18	– 68.9
6	85	–	15	24	– 121.1
7	95	–	5	–	+ 16.5

[1] Belgorod State Technological Academy of Construction Materials, Belgorod, Russia.

0361-7610/00/0304-0084$25.00

The glasses obtained had various tints: from yellow-green (mixture 1), green (2, 3), and green-blue (7) to yellow-brown (4, 5) and black (6). Their spectral characteristics are shown in Fig. 1. Correlating the glass color range with the batch ROP scale, we can see a regularity, which can be explained based on the coloring mechanisms acting in the $Na_2SO_4 - C - Fe_2O_3$ system (Fig. 2).

The ROP of the glass batch evidently has an effect on the state of equilibrium $Fe^{2+} \rightleftarrows Fe^{3+}$ in the melt and, accordingly, on the glass tint. With highly oxidizing potentials (ROP above + 120), the iron in the melts is mainly present in the form of Fe^{3+}, which causes the yellow-green tint in the glass. With ROP values ranging from – 20 to + 120, the iron exists in the form of Fe^{2+} and Fe^{3+} ions, and the superposition of blue and yellow colors yields various shades of green. In the case of reducing batch potentials (ROP from – 20 to – 120), the equilibrium is shifted toward the formation of Fe^{2+} ions, which causes a blue tint or, in the presence of Fe^{3+} ions, a bluish-green tint, which is characteristic of mixture 7 with the minimum sodium sulfate content. Such pigmentation is desirable in heat-shielding glass. In the remaining mixtures with reducing potentials (4 – 6), in addition to ionic tinting, other coloring mechanisms are manifested: tinting by iron sulfide and the amber chromophore



since in the presence of sodium sulfate and an excess of the reducing agent (coal), sulfur appears in the melt in the form of sulfides [2]:

$$SO_4^{2-} + C \rightarrow SO_2 + CO_2;$$

$$SO_4^{2-} + 2C \rightarrow \frac{1}{2} SO_2 + 2CO_2;$$

$$\frac{1}{2} S_2 + C + O^{2-} \rightarrow S^{2-} + CO.$$

The intensity of glass tinting by iron sulfide and the chromophore is very high, as a consequence of which the glass acquires a yellow-brown, a brown, or even a black tint. Since the amber chromophore can appear only in the case of the simultaneous presence of Fe^{3+} and S^{2-} ions, the authors believe that this can occur in melts produced from batches whose ROP is between – 20 and – 60.

Thus, the tint of the glasses considered is the result of three tinting mechanisms manifested to a greater or lesser extent depending on the batch ROP.

The effect of cullet on the batch ROP and the glass tint was evaluated based on mixture 3, whose batch ratio of oxidizing and reducing agents is nearest the same parameter in industrially produced green container glasses and whose

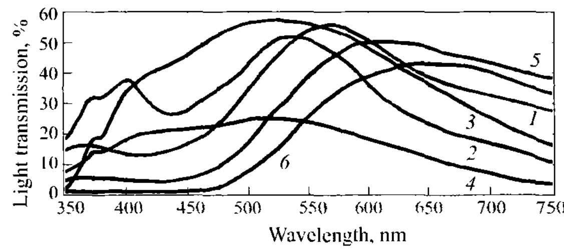


Fig. 1. Spectral characteristics of the glasses considered: *1* – *6*) mixture numbers.

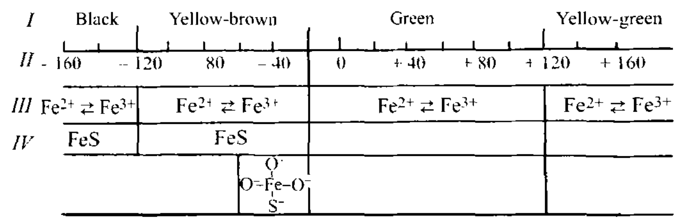


Fig. 2. Batch ROP and glass tinting mechanisms (the boundaries are established by the authors and are, to a certain extent, arbitrary): *I*) glass tint; *II*) ROP; *III*) type of reaction; *IV*) additional tinting components (formed in the course of melting).

batch ROP is near the optimum value [2]. Recycled cullet was introduced into batch 3 in the amount of 30, 50, and 70%. Since the cullet was produced under laboratory conditions, it was considered to be redox neutral.

The calculated ROP values of mixture 3 with a cullet content of 30, 50, and 70% amounted to 24.85, 17.75, and 10.65, respectively, i.e., they decreased in proportion to the decrease in the batch content. It was assumed that such variation in the ROP would not significantly affect the glass color. Indeed, glasses containing these quantities of cullet and melted under the same conditions as glass 3 were tinted green, and their spectral characteristics did not differ from the transmission spectrum of glass 3.

It should be noted that the industry frequently uses cullet that contains reducing agents (organic liquids, paper, cardboard, metal inclusions, etc.). Its effect on the batch ROP (especially when more than 30% cullet is introduced) can be significant and should necessarily be predicted. This can be accomplished by determining the chemical requirement in oxygen both by the cullet and by batches with different batch : cullet ratios [4]. Knowing the value of the cullet ROP, it is possible to maintain this potential at a constant level. Otherwise, introduction of a substantial amount of recycled cullet can disturb the stability of the glass-melting process and the glass tint.

The authors believe that the studies performed clearly show the extent of the effect of the batch ROP on the tint of iron-containing glasses and are ready to assist in introducing constant monitoring of this parameter at glass factories, in particular, factories for production of tinted container glass.

REFERENCES

1. W. Simpson and D. Myers, "The redox number concept and its use by the glass technologist," *Glass Technol.*, **19**(4), 82 – 85 (1987).
2. Yu. A. Guloyan, K. S. Katkova, T. I. Balandina, and A. G. Belyaeva, "Redox characteristics of batches and features of container glass melting," *Steklo Keram.*, No. 11, 4 – 5 (1990).
3. L. M. Khmel', V. A. Fedorova, N. A. Ivakhina, and G. V. Tsokurenko, "Relationship between the batch redox potential and the glass color," *Product. Studies Glass Silicate Mater.*, Issue 10, 57 – 62 (1990).
4. N. T. Lipin, N. A. Orlova, and N. A. Pankova, "Evaluation of the redox potential of glass batches," *Steklo Keram.*, Nos. 11 – 12, 12 – 13 (1993).